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A novel chemical sensor with multiple all-solid-state electrodes and its application in freshwater environmental monitoring

A chemical sensor with multiple electrodes and its application

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Abstract

Freshwater quality detection is important for pollution control. Three important components of water quality are pH, ammonia and dissolved H_2S and there is an urgent need of a high-precision sensor for simultaneous and continuous measurement. In this study, all-solid-state electrodes of Eh, pH, NH_4^+ and S^{2-} were manufactured and mounted to a wireless chemical sensor with multiple parameters. Calibration indicated that pH electrode had a Nernst response with slope of 53.174mV; NH_4^+ electrode had a detection limit of 10^{-5}mol/L (Nernst response slope of 53.56mV between $10^{-1}$to 10^{-4}mol/L). Ag/Ag2S has a detection limit of 10^{-7}mol/L (Nernst response slope of 28.439mV). The sensor was cylindrical and small with low power consumption and low storage demand to achieve continuous *in-situ* monitoring for long periods. The sensor was tested for 10 days in streams at Trawsgoed Dairy farm in Aberystwyth, UK. At the intensively farmed Trawsgoed, the concentration of NH_4^+ in the stream rose sharply after the application of slurry to adjacent fields. Further, the stream was overhung with extensive vegetation and exhibited changes in pH, which correlated with photosynthetic activity. Measurements of S^{2-}were stable throughout the week. Our data demonstrates the applicability of our multiple electrode sensor.

Key Word

Multiple electrode sensor; water environment; in-situ monitoring; Ammonium

Introduction

Globally, agriculture is the largest user of fresh water but is also a source of contamination through chemical runoff. Within freshwater, pH, ammonia and dissolved H_2S are three important indicators of quality. pH is an important measurement of water chemistry and reflects both characteristics of the underlying bedrock and the amount of plant growth and organic material. The latter reflects the release of CO_2 as a result of the decomposition of organic matter and also active respiration, both of which leads to the formation of carbonic acid (H_2CO_3). Plant and algal growth also reflects run-off of nitrogen (N)-fertilizers, whether synthetic or as biological wastes; leading to the eutrophication of water courses (Ip et al., 2004). These N inputs are reduced to free ammonia(Xu et al., 2008). Dissolved H_2S can originate from various sources (coal-based power plants, natural-gas processing, refineries, smelter operation) and can be regarded as a major air pollutant entering the atmosphere and causing acid rain (Primavera et al., 1998). Continuous measurements of dissolved H_2S in water is in need to monitor any accidental releases, particularly from industrial sources (Miloshova et al., 2003). Therefore, monitoring pH, dissolved H_2S and ammonia; ideally continuously, is very important for the agricultural water environment, drinking water and fresh water. *In situ* is a particularly attractive target as some ions in water solution are unstable and easily change to other forms.

The traditional methods for ion measurement include ion chromatography (Rey et al., 1998), fluorometry, spectrophotometry (Goyal et al., 1988) and titration(He, 2000). However these methods are time-consuming and cannot be use for continuous *in-situ* monitoring. Ion selective Electrodes (ISEs), that give a potentiometric signal that obeys the Nernst equation, are currently attracting considerable attention (Mikhelson, 2013). ISEs have a high selectivity to certain ion, and are able to detect low concentrations. Further, ISEs are applicable for *in-*

situ monitoring due to their quick response time(Michalska, 2012). The most widely used ISEs are glass electrodes (Gonçalves et al., 2011; Mikhelson, 2013), which contain an internal reference solution. However, these are difficult to miniaturize and are easy to be damage (Chen et al., 2007; Cheng et al., 2011). The development of all-solid-state electrodes represents a considerable recent improvement (Cattrall & Freiser, 1971; Mikhelson, 2013). They have a lower resistivity and smaller than glass electrodes and have eliminated the need for an internal reference solution. The high performance of all-solid-state electrodes makes it possible to integrate these other electrodes for long-term continuous *in-situ* monitoring in water environment.

In this study, we describe the construction of all-solid-state electrodes for Eh, pH, NH_4^+ and S^{2-}, mounted to a wireless chemical sensor with multiple parameters. We demonstrate the sensors efficacy in the continuous *in-situ* measuring of Eh, pH, NH_4^+ and S^{2-}in freshwater streams in agricultural active farm (Trawsgoed, UK; 52°20′ 38″ N, 3°57′ 4″ W). Thus, extensive use of this sensor could allow the monitoring of agricultural runoff in varying environments.

Methods

Electrode construction and sensor design

Ir/$Ir(OH)_x$-pH electrode preparation and lab test

The Ir wires were ultrasonically cleaned in a HCl bath and then rinsed in deionized water. In three-electrode system of the CHI760D electrochemical workstation, the Ir electrode was used as the working electrode, the Ag/AgCl electrode as the reference electrode and the Pt electrode as the auxiliary electrode. Cyclic voltammetry (CV), with scanning in 5% LiOH solution (0.1 M), was used to form Ir electrode with a layer of $Ir(OH)_x$ film(Zhang et al., 2017).

pH buffer solutions of 4.00, 6.86, 9.18 were used to calibrate the $Ir/Ir(OH)_x$-pH electrode. The pH electrode was calibrated using a CHI760D electrochemical workstation.

NH_4^+ electrode preparation and lab test

A Ag wire was polished with alumina powder and ultrasonically cleaned in a HCl bath. This was rinsed in deionized water and dried in open air. A nano-Ag layer was electroplated to Ag wire for better conductivity. The anode and the cathode of the electroplating system were all Ag wires. A solution of 0.1M $AgNO_3$ was used as the electrolyte.

The conductive polyaniline (PANI) layer was formed by the three-electrode system. Cyclic voltammetry (CV) method was used in 0.1M aniline hydrochloride. Then the wire was dipped in saturated solution of copolymer aniline(CPANI) and 2,5-dimethoxyanilineas the second layer. Finally, Ammonium ionophore I (6.9%), Potassium tetrakis (4-chlorophenyl) borate (0.7%) and 2-Nitro phenyloctyl ether (92.4%) was dissolved in N,N-Dimethyl formamide (DMF) and the wire dipped into this solution to form the third layer(Huang et al., 2015).

A series of NH_4Cl solution from 1×10^{-5} to 1×10^{-1} M were prepared. The NH_4Cl solution consisted of 0.5349 g NH_4Cl and made up to 100 mL in volumetric flask with deionized water to obtain a 1×10^{-1} M NH_4Cl solution. 1×10^{-2} M to 1×10^{-5} M NH_4Cl solution were stepwise diluted by the 1×10^{-1} M standard NH_4Cl solution with deionized water. The NH_4^+ electrode was calibrated using a CHI760D electrochemical workstation.

Ag/Ag_2S electrode preparation and laboratory testing

A 3 cm Ag wire was polished and electroplated with a nano-Ag layer using the same method as described in 2.2 and then immersed to the 0.1M Na_2S solution for 10 min. Ag_2S formed the outmost layer of the electrode(Ding et al., 2015).

A series of Na_2S solutions ranging from 1×10^{-7} to 1×10^{-1} M were prepared. To avoid S^{2-} oxidation, a sulfur antioxidant buffer (SAOB) was prepared in place of deionized water when preparing the Na_2S solution. Stocks of 1L of SAOB contained 80 g of NaOH, 35 g of ascorbic acid (VC), 67 g of EDTA-2Na, and 35 g of NaCl. The Na_2S solution consisted of 0.7804g Na_2S and made up to 100 mL in volumetric flask with SAOB to obtain a 1×10^{-1} M Na_2S solution.1×10^{-2} M to 1×10^{-7} M Na_2S solutions were stepwise diluted by the 1×10^{-1} M standard Na_2S solution with SAOB. The Ag/Ag_2S electrode was calibrated using a CHI760D electrochemical workstation.

Multiple-parameter sensor design

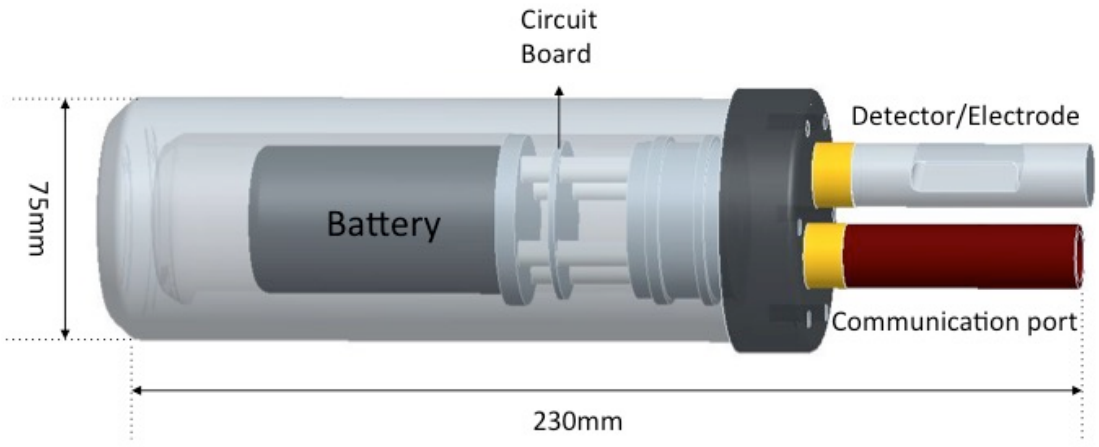


Figure 1 Structural Diagram of Chemical Sensor

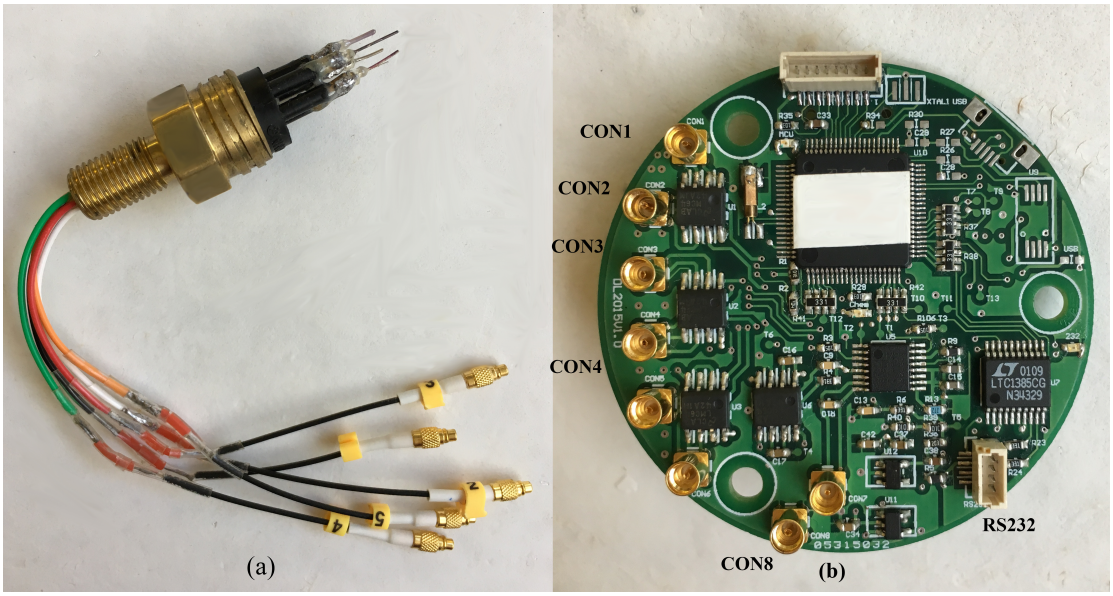


Figure 2 Structure Details (a) Detector part/Electrodes (b)Circuit Board Structure

Figure 1 shows the structural diagram of chemical sensor. The outer shape is a cylinder with a length of 230mm and 75mm in diameter. The outer covering is made up of 30CrMnSi, which is a compound metal which confers added strength to protect the sensor against environmental impacts. The sensor contains a communication port, a detector part outside and a circuit board and a battery. The pH electrode, NH_4^+electrode, Ag/Ag_2S electrode, Eh electrode and Ag/AgCl reference electrode were integrated into the detector part (Figure 2 (a)). The Eh electrode was made of a platinum wire and Ag/AgCl reference electrode was prepared by melting method (Zhong & Yexiang, 1998). To better connect the electrode to the detector part, the platinum wire and Ir wire were connected to Ag wire by gas welding. The exposed metal parts, which connect electrode and electric wire, were wrapped individually by shrinkable tube and an epoxy resin layer to avoid corrosion and short circuiting.

When the sensor is in use and submerged in water, a semi-hollow cap covers the detector part. The semi-open design of the detector part not only guarantees full contact between electrodes and water but also prevent the chemical membrane being damaged by rapid rushing water and greatly avoid biofouling.

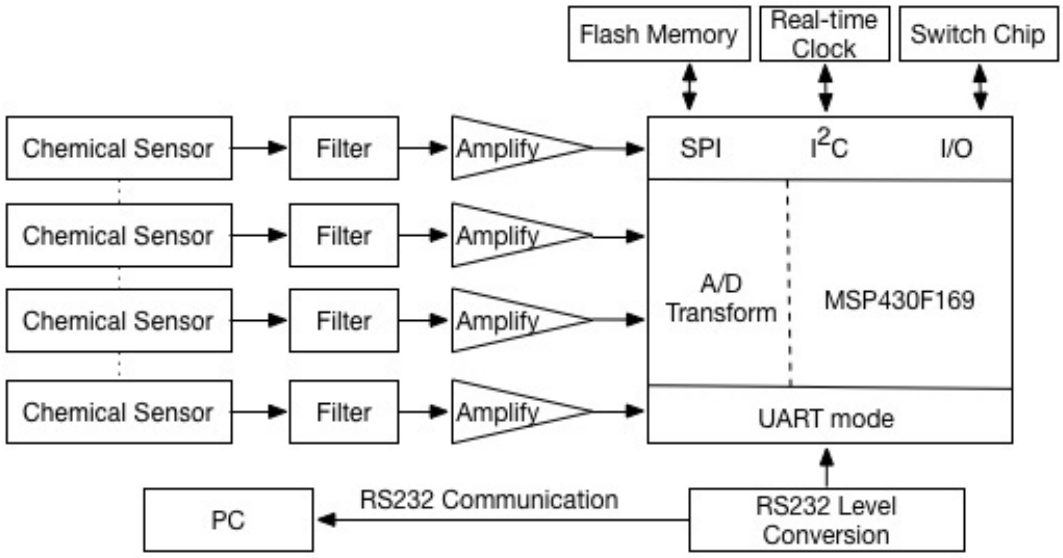


Figure 3 Working Principle of the data acquisition system

Figure 3 illustrates the working principle of the data acquisition system. First, the chemical sensors detect the chemical signals and convert chemical signals into electrical signals, which then go through the filter, are amplified into the main processor, and stored in a Flash memory function. The watertight connector may be linked to the host computer for real-time communication. The whole data collection can be controlled by the host computer's software. The built-in clock and switch chip of the processor were calibrated by the host computer software, which also initiates the sensor's work mode to collect signals. The multi-parameter sensor can then be disconnected from the host computer in the start the work mode of the processor and used for in-situ observations. At the end of the observation period, the multi-parameter sensor and the host computer can be reconnected to read the stored data through the watertight connector.

Figure 2 (b) shows the structure of the circuit board. Each electrode was connected to a certain port from 'CON1' to 'CON 4' with a reference electrode at the center, which was connected to 'CON 8'. 'RS232' is the communication interface, connecting to signal lines. According to the circuit board design, the real-time data can be stored in a Flash chip when carrying out fieldwork and retrieved later after connecting to software.

The frequency of data collecting can be set at a minimum of 1s or greater intervals. Therefore, the sensor can be used in multiple environments without constraints of distance as the sensor works and store data independently without connecting to a host computer. The two system mode, sleep mode and work mode, consume 1.0mA and 3.5mA electric current respectively. The input impedance of the system is $10^{13}\ \Omega$(25℃), which guarantee long-term use with two AA Li batteries. The data is stored in a Flash chip with 128M bit storage capacity as internal storage. If measuring frequency is set as once per 1 minute, the storage can guarantee 2 years monitoring. When the storage is full, new data will cover old data automatically. Due to its lower power consumption and low storage demand, the sensor can achieve continuous in-situ monitoring for at least 6 months. The circuit board and the batteries are sealed in the cylinder made up of 30CrMnSi, no harmful to the surrounding environment.

Life cycle of whole system is about 2 years, needs service to change electrodes and batteries every 6 months.

Polyaniline (PANI) and Silver nano particle, which are bacteriostatic are used for preparation of NH_4^+ and Ag_2S electrodes respectively(Tian, 2010; Zongming Xiu, 2012). The 0.25mm diameter Ir wire used for pH electrode is thinner and hard to be adhered. This avoid problem of biofouling in lifetime.

Field trial locations

A ten-day fieldwork was conducted between September 17- 26thSeptember 2016 at Trawsgoed Farm, Aberystwyth, UK. Trawsgoed Farm is the location of a 350-cow commercial dairy herd. As such the farm produces a large volume of slurry from its livestock. Several ditches stretch across the farm and feeds into the River Ystwyth some 28 km from its mouth. Given this potential for wide-ranging impact on local water quality, it is appropriate to engage in monitoring streams around this farm.

Figure 4 Sensor Position in Trawsgoed Farm

The multiple-parameter sensor, which can detect Eh, pH, NH_4^+ and S^{2-}, was positioned in the ditch of the farm (52°20′ 38″ N, 3°57′ 4″ W). The position has been indicated as red spot in Figure 4. The ditch was about 0.5m deep and 1.0m surrounded with green planets. During the field trial, slurry was applied by shallow injection into the farmland adjacent to this stream on the Sept 18th and Sept 19th. As an independent measure of pH, this was measured at a position close to sensor using a Thermo Scientific Orion, ROSS pH Electrode. pH was measured in around midday on Sep. 19th, 20th, 21st, 22nd, 23rd, 24th, 25th, 26th.

To understand the daily variation of chemical parameters, the sensor was set to collect data every 1 minute during the field trial. The sensor was taken back and connected to host computer to extract the stored data at the end of the each period

of fieldwork. The obtained potential value was converted to concentration value based on the calibration result. To reduce the effect of any abnormal data, the average of every half an hour was calculated based on the obtain 1 minute measurements.

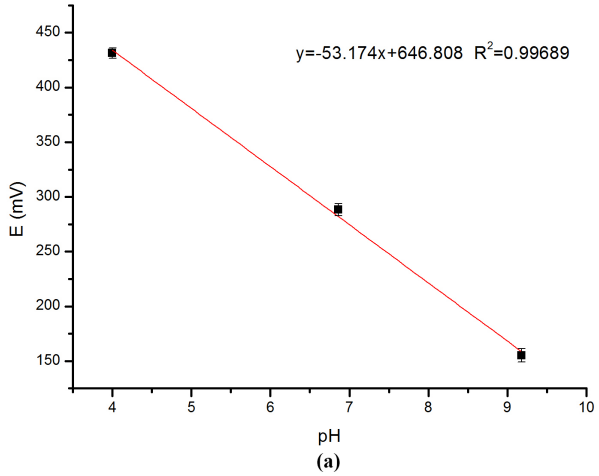
To allow for the effect of temperature, *in situ* pH data was converted to 25°C pH using the following formula:

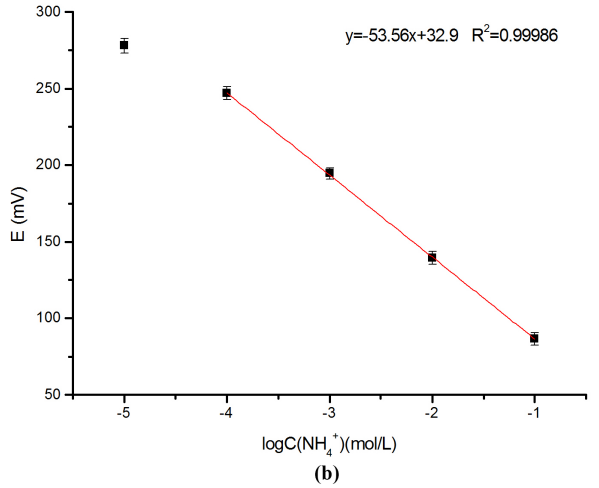
$$pH_{25} = pH_{in\ situ} - 0.0151 \times (25 - T)$$

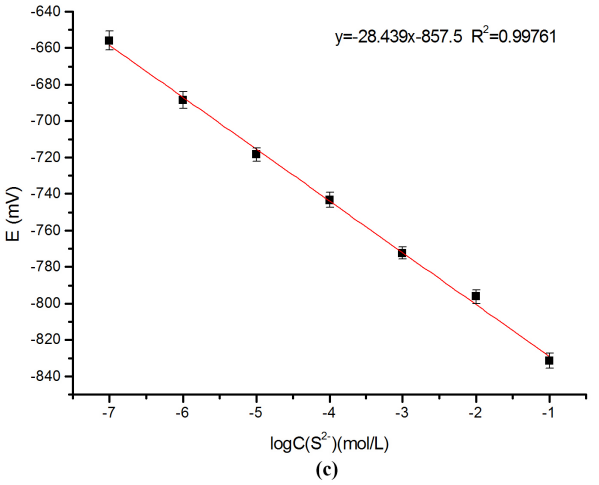
where T is temperature from Aberystwyth weather website("Past Weather in Aberystwyth, Wales, United Kingdom," 2016).

Results and Discussion

Electrode Calibration







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2 Figure 5 Potential-pH response of (a) Ir/Ir(OH)$_x$-pH electrode (b) NH_4^+ electrode (c) Ag/Ag_2S electrode

3 Figure 5 (a) shows the potential-pH response of the Ir/Ir(OH)$_x$-pH electrode. The

slope of the fitting line is 53.174, close to the Nernst theoretical value. The correlation coefficient at $R^2 > 0.996$, indicated good linearity when fitting the calibration curve. Figure 5 (b) shows the calibration results of NH_4^+ electrode in NH_4Cl solution from 10^{-5} to 10^{-1}M. The potential gradient from 10^{-5} to 10^{-4} was a little smaller compared with others, the slope of the fitting line from 10^{-4} to 10^{-1}M was 53.56 with a coefficient $R^2 > 0.998$, which is also close to the Nernst theoretical value. The Ag/Ag_2S electrode has high detection limit. Figure 5 (c) shows the calibration results in Na_2S solution from 10^{-7} to 10^{-1} M. The fitting line was 28.439 with a coefficient $R^2 > 0.997$.

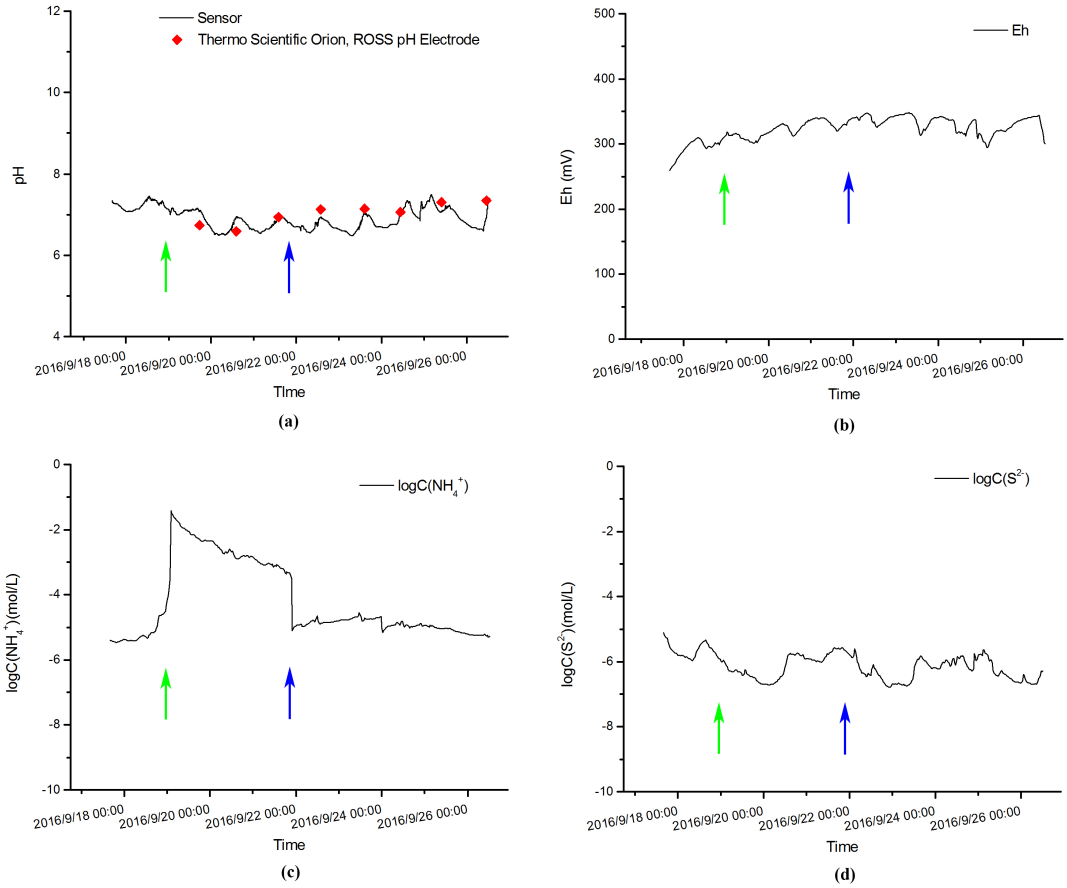

Figure 6 Concentration change between 2016/9/17 and 2016/9/26 in Trawsgoed (a) pH-time (b) Eh(mV)-time (c) log C (NH_4^+)(mol/L)-time (d) log C (S^{2-})(mol/L)-time. The green allow indicates when slurry was applied to adjacent fields and the blue arrow a period of heavy rain.

Measuring environmental pH value change

As an initial indication of sensor performance, the pH detected by the sensor at Trawsgoed farm was compared to that detected by a glass pH electrode with an internal reference solution. The pH values for the measuring period ranged between 6.5 and 7.4 (Figure 6 (a)). Table 1 compared the result of pH value tested by pH probe and sensor the latter showed as red spots in Figure 4. The average difference of pH value between pH probe and Sensor was 0.18, which reveals the accuracy of the pH electrode of the sensor. In table 1, pH given by the probe is in the range between 6.6 to 7.36; while that given by the sensor is between 6.89 to 7.20. It seems that the latter is more stable.

Table 1 Comparison of pH values obtained using the pH probe and Sensor

Time	Temperature (°C)	pH		Variation (%)
		pH probe[1]	Sensor[2]	
2016/09/19 17:33	16.0	6.75	7.08	4.89%
2016/09/20 14:00	18.0	6.60	6.94	5.15%
2016/09/21 13:50	18.0	6.95	6.89	0.86%
2016/09/22 13:44	16.0	7.14	6.94	2.8%
2016/09/23 14:40	17.6	7.16	7.09	0.98%
2016/09/24 10:44	17.7	7.07	7.08	0.14%
2016/09/25 10:00	13.0	7.32	7.07	3.42%
2016/09/26 11:52	13.9	7.36	7.20	2.17%

[1] pH value given by Thermo Scientific Orion, ROSS pH Electrode

[2] pH value given by the sensor

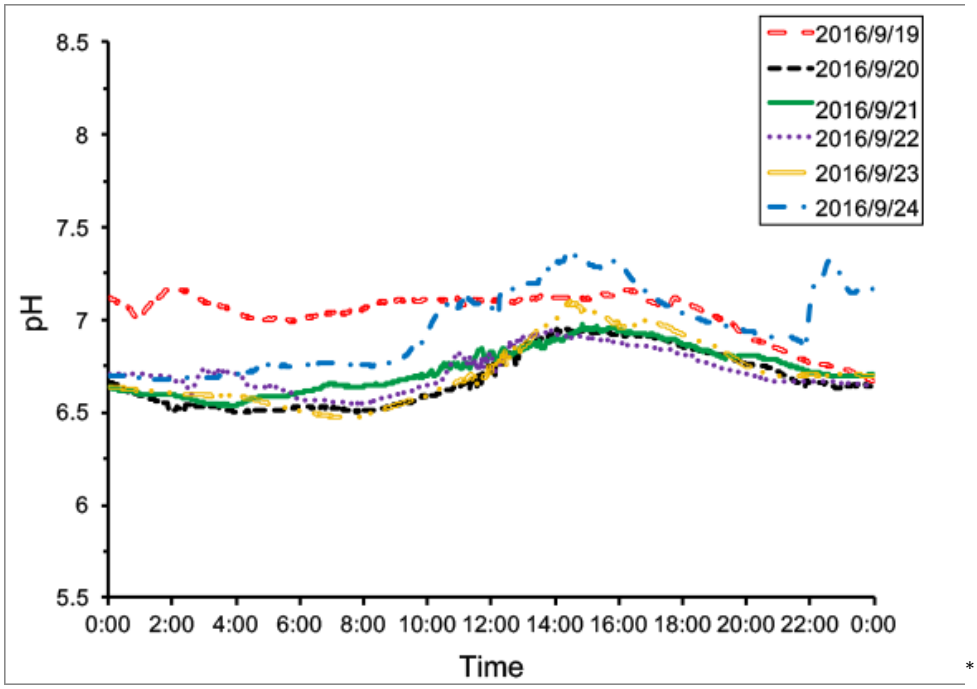

Figure 7 Changes in 24-hour pH value changes in Trawsgoed

Examining the sensor derived pH values over a diurnal cycle indicated a regular daytime rhythm (Figure 7). It decreased to the lowest value at around pH 6.5 at ~ 6:40 AM in the morning and increases to a peak at around 7.2 at 14:00 PM in the afternoon. Given that the sensor was located in an area of dense vegetation, this feature almost certainly reflected the shifting balance between respiration and photosynthesis. At night, plants absorb oxygen and produce carbon dioxide because of respiration to increase of H_2CO_3 in water resulting in a decrease of pH. During daylight, plants absorb carbon dioxide and produce oxygen because of photosynthesis leading to a relative decline in H_2CO_3 and increase in pH. The fact that this pattern was easily detected by the sensor is an indicator of its sensitivity in the detection of pH.

Between pH-Eh.

Comparing Figure 6(a) and Figure 6 (b) shows how pH and Eh show contrasting trends; thus, Eh increases when pH decreases and decreases when pH rises. This

fits the negative correlation functional relationship between Eh and pH(Brookins, 1988):Eh=A-0.059pH, where A is a constant.

NH_4^+ concentration change

The concentration of NH_4^+proved at Trawsgoed farm (Figure 6 (c)) proved to be stable at $\sim 1.0 \times 10^{-5}$M for the first two days of the measuring period. However, immediately after the injection of slurry into neighboring fields, the NH_4^+ concentration rose sharply to 1.6×10^{-2}M (Sep. 19th,2016). During the following days, this concentration appeared to be being diluted due to the continual flow of water in the area so that the NH_4^+ concentration fell progressively to 3.9×10^{-4} M by Sep. 21st. There was a rapidly decrease to 1.6×10^{-5}M which correlated with a rain shower in Sep. 21st evening which would have appeared to accelerate the dilution process. These results clearly indicate that the application of slurry increases the concentration of NH_4^+ in the stream and most likely in the Ystwyth River to which it is a tributary.

4.5 S^{2-}concentration change

The concentration of S^{2-} fluctuated slightly but average to $\sim 1.0 \times 10^{-6}$ M (Figure 6 (d)). This was quite a low concentration, which the application of slurry did not significantly change in the water.

Conclusions

An all-solid-state electrodes of Eh, pH, NH_4^+ and S^{2-} was manufactured and mounted to a wireless chemical sensor with multiple parameters. Under laboratory conditions we demonstrated continuous and simultaneous measurement of Eh, pH, NH_4^+ and S^{2-}.

The sensor was field tested in streams at Trawsgoed farm in Aberystwyth, UK. The result in Trawsgoed indicates that pH value exhibits regular daytime fluctuations due to plant metabolism. The average difference of pH value between a commercial pH probe and the constructed sensor was only 0.18. The trends of pH and Eh stay fitted with the known negative correlation functional relationship between Eh and pH. The concentration of NH_4^+ rose sharply when slurry was applied to neighboring fields.

From above, the electrodes of sensor show high accuracy and sensitivity to certain ions. Regarding to the feature of small volume, less power consumption and low storage demand, the sensor will have a broad application in water environment detection.

Acknowledgements

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